is counterbalanced through a potentiometric circuit made up of the variable resistance,  $n_1$ , and the potentiometer.  $n_2$ . Thereafter, only the potential resulting from the unbalancing of the system feeds a recorder, R. A standard source, P, of potential is used to determine with accuracy the absolute value of the balance point on the recorder.

Resistance. All resistance measurements of the solution were made with a conductivity bridge of Type LKB 3216B modified as follows: A set of decade-resistance units from 0.001 to 1000 ohms increased the precision of the bridge; a series of decade-capacitor units from 0.01 to 1  $\mu$ f. was added to expand the Wagner earth circuit; finally an oscilloscope was substituted for the magic eye. Figure 4 shows how the signal coming from the bridge is filtered and amplified at A, rectified and compressed at K, and finally recorded at R.

Measurement. The cell is filled with ammonium nitrate solution at a temperature very close to that of the bath in which it will be immersed. At thermal equilibrium a balance point is preselected on the chart of the recorder and tied into the potentiometric circuit (Figure 3). Thereafter, the variations of resistance and temperature of the solution in the cell are simultaneously registered on one graph by a two-channel recorder.

The specific conductances for a 0.1D KCl solution reported by Gorbachev (9) were utilized to determine the cell constant which, in the temperature range 25° to 95° C., was found to be unchanged.

### **RESULTS AND DISCUSSION**

Based on the precision of the instruments utilized, the accuracy obtained in the determination of the specific conductance of ammonium nitrate solutions is  $\pm 0.01\%$  of the values shown in Table I. The absolute values are affected by an error of 0.1%, resulting mainly from the quality of standards used for thermocouple calibration.

The behavior of the specific conductance as a function of concentration is similar for all temperatures. The curves show a maximum in the vicinity of 52 weight % NH<sub>4</sub>NO<sub>3</sub>. Campbell's results (3, 4) have been plotted in a similar manner (broken lines). The maxima found are in very good agreement with the present data (Figure 5).

## LITERATURE CITED

- (1)Campbell, A.N., Bock, E., Can. J. Chem. 36, 330 (1958).
- Campbell, A.N., Friesen, R.J., Ibid., 37, 1288 (1959). (2)
- (3)Campbell, A.N., Gray, A.P., Kartzmark, E.M., Ibid., 31, 617 (1953).
- Campbell, A.N., Kartzmark, E.M., Ibid., 30, 128 (1952). (4)
- Campbell, A.N., Kartzmark, E.M., Can. J. Res. 28B, 161 (5)(1950).
- (6)Campbell, A.N., Kartzmark, E.M., Bednas, M.E., Harrar, J.T., Can. J. Chem. 32, 1051 (1954). Dole, M., "Experimental and Theoretical Electrochemistry,"
- (7)p. 59, McGraw-Hill, New York, 1935.
- Glasstone, S., "Introduction to Electrochemistry," p. 40, Van Nostrand, New York, 1942. Gorbachev, S.V., Kondratev, V.P., Zh. Fiz. Khim. 35, 1235
- (9)(1961).
- "International Critical Tables," Vol. VI, p. 240, McGraw-(10)Hill, New York, 1929.
- Scatchard, G., Prentiss, S.S., J. Am. Chem. Soc. 54, 2696 (11)(1932).
- (12) Sisi, J.C., Dubeau, C., J. CHEM. ENG. DATA 11, 58 (1966).

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# **Electrolytic Conductance and Ionic** Association of Several Salts in Ethanol-Water Mixtures

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The electrolytic conductance of lithium chloride, potassium picrate (KPi), potassium tetraphenylborate (KBPh4), triisoamyl-n-butylammonium picrate (TABPi), and triisoamyl-n-butylammonium tetraphenylborate (TAB BPh4) was measured at 25°C. over the range of ethanol-water mixtures where ion-pair association was expected. Limiting equivalent conductances and ion-pair association constants for the electrolytes were derived using either the Fuoss-Onsager theory or the Shedlovsky function. Limiting equivalent conductances for the single ions were calculated on the basis of the Coplan-Fuoss assumption. Ion-size parameters are reported for the solutions analyzed by the Fuoss-Onsager theory.

THE PROPERTIES of triisoamyl-n-butylammonium (TAB) and of tetraphenylborate (BPh<sub>4</sub>) salts in different solvents are of special interest. According to Coplan and Fuoss (3), the limiting equivalent conductances of  $TAB^+$ and BPh<sub>4</sub> ions in any given solvent can be equated, making it possible to calculate the conductances of other single ions. Popovych (14) assumed that the above two ions expe-

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rience equal changes in their standard free energy of solvation upon transfer from water to nonaqueous solvents and proposed that they be used as reference ions for the establishment of a scale of single-ion medium effects. Lithium chloride was studied here because of its potential use for varying the ionic strength of ethanol-water solutions in the determination of activity coefficients. Its conductance was reported previously for 100% ethanol (12). The main objective of the present study was to determine the degree of ionic association for electrolytes in those ethanol-water mixtures where it was appreciable. No attempt was made to study systematically the conductance in solvent ranges where no ion association was expected.

## EXPERIMENTAL

Preparation and purification of potassium picrate (KPi) and potassium tetraphenylborate (KBPh<sub>4</sub>) have been described (15). Triisoamyl-n-butylammonium tetraphenylborate (TAB BPh<sub>4</sub>) and triisoamyl-n-butylammonium picrate (TABPi) were synthesized and purified essentially by the method of Coplan and Fuoss (3). TABPi was also prepared by direct combination of equimolar methanolic solutions of triisoamyl-n-butylammonium iodide (TABI) and picric acid at about 50°C. The crude product was precipitated by addition of water and cooling. It was separated immediately from the reaction mixture to prevent oxidation of the iodide by the picrate. The product was recrystallized by dissolving in hot methanol, adding just enough water to make the solution cloudy, and then redissolving the precipitate with a minimum of hot methanol. The crystals which separated upon cooling were dried in vacuo at 60°C. for 24 hours. Baker analyzed LiCl was purified by double recrystallization from conductivity water, followed by drying at 110°C. for 48 hours. The dried salt was stored and transferred to tightly stoppered weighing bottles in a dry box. For use in the determination of the conductance-cell constant, Baker analyzed potassium chloride was recrystallized twice from distilled water and once from absolute ethanol, followed by drying at 110°C. for 24 hours. All electrolytes were recrystallized once more immediately prior to the determination of their conductances.

U.S.P. 95% ethanol was purified by double distillation from an all-borosilicate glass distillation apparatus with a 30-cm. Vigreux column. About 5 liters were taken for each distillation: the first 1.5 liters were rejected and the middle fraction of about 2.5 liters was collected. The fresh distillate had a density of 0.8067 gram per ml. at  $25^{\circ}\,\mathrm{C}.$ corresponding to 92.3 weight % ethanol and a specific conductance of less than  $1 \times 10^{-7}$  mho per cm. In the purification of 100% ethanol, approximately 5 liters of U.S.P. absolute alcohol were refluxed over magnesium ethoxide for 12 hours while a slow stream of nitrogen was passed through the charge, and then distilled. The middle fraction of about 2.5 liters collected for use had a specific conductance of the order of  $10^{-8}$  mho per cm. and a density of 0.7851 gram per ml. at 25°C. The density compares favorably with its literature values of 0.7850 (8) and 0.7851(4). Deionized water with a specific conductance of  $3 \times 10^{-7}$  mho per cm. was used.

Ethanol-water mixtures were prepared by measuring out, either by weight or by volume, approximate amounts of ethanol and water. The density of a resulting mixture at  $25^{\circ}$  C. was determined by weighing 100 ml. of it in a calibrated volumetric flask. Duplicate determinations were made and the weight was corrected to vacuum. The exact composition of a mixture was then interpolated from a large-scale plot of density vs. weight per cent ethanol prepared from literature data (13).

Solutions of the electrolytes were freshly prepared by weight and corrected to vacuum. Molar concentrations of the solutions were calculated from the weights and from the density of the dilute solutions taken to be equal to the density of the solvent. The measurements were carried out on a Wayne-Kerr Model B-221 Universal bridge and the Model Q-221 low-impedance adapter. This bridge reads out conductance directly with an accuracy of 0.1%. The conductance cell contained very slightly platinized platinum electrodes with a cell constant of 0.010017 cm.<sup>-1</sup> based on the Jones and Bradshaw aqueous 0.01 demal KCl standard (11). The cell was of the pipet type sealed at the bottom by a water-tight ground-glass cap. Before each run the conductance cell was thoroughly washed with the given solvent. Prior to each equilibration, the cell was rinsed with the solution whose conductance was to be measured. It was then equilibrated successively with three fresh portions of the solution until the consecutive readings on the third portion taken at 15-minute intervals agreed to about 0.05%. Throughout the measurements, the cell was immersed in a water bath at 25°C. controlled to  $\pm 0.003$ °C. by a Yellow Springs Instrument Co. Model 72 proportional temperature controller. The absolute temperature of the bath was determined to  $\pm 0.01^{\circ}$  by means of an NBS certified thermometer.

## RESULTS AND DISCUSSION

Table I lists the necessary physical properties of ethanolwater mixtures actually studied. The percentage of ethanol by weight, w, was obtained from the measured density,  $d_o$ , by interpolation of literature data (13). Literature values were also interpolated to obtain the viscosity,  $\eta$  (10), and the dielectric constant, D (2), of each solvent. Also tabulated are the measured specific conductances of solvents,  $k_o$ . Tables II to VI give the molar concentrations, C, and the equivalent conductances,  $\Lambda$ . Limiting equivalent conductances  $\Lambda_o$  and ion-pair association constants  $K_A$  were derived from these data with the aid of the Fuoss-Onsager theory (4, 5) or the Shedlovsky modification of the Ostwald dilution law (6, 16). The Fuoss-Onsager equation assumes the form

$$\Lambda = \Lambda_{\circ} - SC^{1/2}\gamma^{1/2} + EC \gamma \log C\gamma + JC\gamma - K_{A}C\gamma f_{\pm}^{2}\Lambda - F\Lambda_{\circ}C \quad (1)$$

for associated electrolytes and the form

$$\Lambda = \Lambda_o - SC^{1/2} + EC \log C + JC - F\Lambda_o C$$
<sup>(2)</sup>

for unassociated electrolytes. The Shedlovsky function (for associated electrolytes) is;

$$\frac{1}{\Lambda S_{(z)}} = \frac{K_A C \Lambda f_{\pm}^2 S(z)}{\Lambda_o^2} + \frac{1}{\Lambda_o}$$
(3)

Throughout these equations the symbols are those used in the monograph by Fuoss and Accascina (4). Equation 1 was solved by the (graphical) y-x method described by Fuoss *et al.* (1, 4, 5) and Equation 2, by the method of least squares. The evaluation of y and x, which requires successive approximations, and all other calculations in this study were carried out on an IBM 1620 computer using Fortran programs.

Table I.	Properties o	f Ethanol-W	ater Mixture	s at 25° C.
w	$10^7 k_o$	d。	D	100 $\eta$ , Poises
100.0	0.8 - 1.4	0.7851	24.3	1.101
92.3	0.7 - 2.4	0.8067	27.1	1.351
86.6	2.8	0.8219	29.6	1.530
84.5	2.9	0.8276	30.5	1.599
81.8	3.2	0.8340	31.9	1.680
80.8	3.1	0.8367	32.7	1.708
80.1	2.0	0.8388	32.7	1.730
79.3	3.1	0.8407	33.1	1.755
77.2	4.2	0.8453	34.2	1.810
70.8	5.1	0.8612	37.5	1.998
68.2	2.2	0.8672	38.9	2.060
65.5	2.2	0.8742	40.4	2.125
62.0	1.5	0.8828	45.0	2.195
57.1	3.5	0.8942	45.0	2.280
53.3	2.0	0.9022	47.2	2.330
53.1	2.9	0.9026	47.3	2.317
51.0	2.9	0.9073	48.5	2.359
43.5	3.2	0.9268	52.9	2.386
27.7	4.0	0.9543	62.4	2.138

Table II. Conductance of LiCl in Ethanol-Water Mixtures at  $25^{\circ}\,\mathrm{C}.$ 

92.3 Etha	% nol	86.6 Etha	% nol	77.2 Etha	% nol	68.2 Etha	% nol	57.1 Etha	% nol	43.5 Etha	% nol
10 <sup>4</sup> C	Λ	$10^{4}C$	Λ	$10^4C$	Λ	10 <sup>4</sup> C	Λ	10 <sup>4</sup> C	Λ	10⁴ <i>C</i>	Λ
3.6380	37.50	3.9699	37.45	7.8546	36.81	11.0221	37.10	8.4602	38.95	9.1577	43.14
4.6376	37.16	6.9268	36.71	15.6832	35.76	15.9207	36.56	10.4471	38.75	13.1461	42.81
11.0060	35.58	9.8553	36.10	18.9695	35.41	19.2569	36.30	14.3927	38.39	15.8197	42.60
13.8638	35.03	12.0105	35.73	23.8040	34.94	23.4666	35.88	20.9056	37.93	19.8738	42.35
15.7227	34.71	14.8248	35.28	26.7699	34.69	26.7491	35.65	24.9027	37.64	22.4354	42.21
18.2485	34.30	17.0150	35.00	31.5632	34.30	32.5517	35.21	31.1280	37.25	26.3169	41.94
22.7350	33.68	19.8319	34.62	39.3127	33.74	41.0944	34.69	36.7819	36.98	32.5144	41.65
		24.3599	34.07					41.0088	36.80		
								52.1134	36.27		

## Table III. Conductance of KPi in Ethanol-Water Mixtures at 25° C.

100% E	Ithanol	92.3% E	thanol	84.5% E	Ethanol	79.3% Ethanol	
10 <sup>4</sup> C	Λ	10 <sup>4</sup> C	Λ	$10^{4}C$	Λ	10 <sup>4</sup> C	Λ
3.0588	45.19	3.3101	43.26	2.9212	40.78	2.3209	39.53
3.3347	44.92	3.6242	43.05	3.2568	40.64	2.5822	39.38
3.5146	<b>44.72</b>	3.8503	42.99	3.6471	40.60	3.1099	39.26
3.8060	44.44	4.1068	42.78	3.7690	40.53	3.5586	39.21
3.9717	44.28	4.3592	42.70	4.0508	40.46	3.8446	39.13
4.2874	43.98	4.7094	42.50	4.3275	40.34	4.1017	38.99
4.5302	43.74	4.9381	42.44	4.6527	40.26	4.3673	39.05
4.7869	43.53	5.2649	42.26	4.8659	40.20	5.1269	38.83
5.0864	43.28	5.5307	42.13	5.1522	40.18		
65.5% <b>E</b>	Ethanol	62.0% Ethanol		53.1% Ethanol		27.7% Ethanol	
10 <sup>4</sup> C	Λ	10 <sup>4</sup> C	Λ	$10^4C$	Λ	$10^4C$	Λ
3.7840	37.54	4.9825	37.74	3.1793	38.48	2.6757	50.76
4.0459	37.54	7.1359	37.47	3.7060	38.41	2.9830	50.71
4.4192	37.40	9.5502	37.20	3.9563	38.42	3.2357	50.64
4.7035	37.42	14.694	36.82	4.2206	38.36	3.5604	50.64
5.0630	37.38	16.898	36.60	4,4975	38.34	3,7277	50.69
5.3644	37.39	19.201	36.47	5.3246	38.32	3.8953	50.52
5.6320	37.26	21.624	36.33			4.1602	50.56
5.9579	37.19	24.503	36.18			4.9517	50.57
6.3569	$\cdot 37.27$						

# Table IV. Conductance of KBPh<sub>4</sub> in Ethanol-Water Mixtures at 25° C.

100% E	thanol	92.3% I	Ethanol	80.1% H	Ethanol	70.8% H	Ethanol	51.0% H	Ethanol
$10^{4}C$	Λ	$10^{4}C$	Λ	$10^4C$	Λ	$10^4C$	Λ	10 <sup>4</sup> C	Λ
1.2469	41.94	1.9438	39.03	2.0082	34.76	4.3500	33.10	3.4816	34.97
1.3454	41.79	2.4237	38.89	2.5556	34.76	4.7751	33.08	3.6894	34.94
1.4333	41.54	2.6202	38.83	2.9813	34.71	5.2192	33.02	3.9620	34.88
1.5551	41.47	2.7873	38.72	3.1157	34.67	5.4491	32.91	4.2161	34.91
1.8048	41.30	2.9374	38.68	3.2981	34.67	6.2614	32.88	4,4454	34.84
1.9998	41.18	3.1042	38.59	3.4754	34.67	6.5940	32.86	4.6876	34.82
		3.3022	38.56	3.7010	34.59	7.1747	32.72	4.9738	34.79
						7.5528	32.71		

Table V. Conductance of TABPi in Ethanol-Water Mixtures at  $25^{\circ}\,\text{C}.$ 

100% Ethanol		92.3% Et	92.3% Ethanol		thanol	53.3% Ethanol	
10 <sup>4</sup> C	Λ	10 <sup>4</sup> C	Λ	$10^4C$	Λ	$10^4C$	Λ
5.9568	40.13	2.3170	36.42	5.9836	30.10	5.9984	22.35
7.8480	39.18	5.7402	34.93	7.7143	29.73	8.2202	22.08
10.181	38.24	7.1084	34.46	10.270	29.23	12.088	21.68
12.049	37.50	7.9432	34.22	12.056	28.90	14.067	21.50
14.140	36.81	9.3462	33.78	14.419	28.52	17.824	21.18
16.096	36.21	11.678	33.17	16.751	28.18	20.275	20.99
18.158	35.65	13.669	32.72	18.421	27.95	23.232	20.76
20.464	35.05	16.118	32.18	20.515	27.68	26.020	20.57
22.515	34.56	18.692	31.70	22.230	27.48	29.075	20.36

Table VI. Conductance of TAB BPh<sub>4</sub> in Ethanol-Water Mixtures at 25° C.

100% Ethanol		92.3% I	Ethanol	80.8% Ethanol		
$10^{4}C$	Λ	10 <sup>4</sup> C	Λ	$10^{4}C$	Λ	
2.9670	35.78	2.0425	30.68	2.4138	25.22	
3.2637	35.59	2.2442	30.57	3.0157	25.05	
3.5108	35.42	2.4098	30.48	3.3259	24.98	
3.7734	35.25	2.6014	30.38	3.5042	24.94	
4.0337	35.08	2.9468	30.21	3.7169	24.86	
4.2911	34.94	3.1818	30.10			
4.5974	34.72	3.3326	30.04			
4.8476	34.54	3.5578	29.95			
5.0714	34.44					
5.4135	34.22					

The viscosity term  $F_{\Lambda_o}C$  in Equations 1 and 2 was considered to be negligible for all the solutions and was not included in the calculations. In the case of LiCl this was justified because of the small size of the ions involved. For other solutions, the viscosities were experimentally determined to be practically the same as those of the pure solvents. In the calculations via Equation 1, the activity coefficient  $f_{\pm}$  was first approximated from the Debye-Hückel law using an estimated value for both the degree of dissociation,  $\gamma$ , and the ion-size parameter, a. Both  $\gamma$  and a were then refined and recycled by successive approximations, where the ion-size parameter was being obtained from the coefficient J and therefore designated  $a_J$ . In the Shedlovsky calculations, the activity coefficient was calculated from the limiting Debye-Hückel law, again using successive approximations with respect to  $\gamma$ .

Equation 2 was used to analyze the data for KPi in 27.7, 53.1, 62.0, and 65.5 weight % ethanol and for KBPh<sub>4</sub> in 51.0, 70.8, and 80.1 weight % ethanol (unassociated electrolytes). For the remaining (associated) electrolyte solutions, either Equation 1 (LiCl, TABPi) or Equation 3 (KBPh<sub>4</sub>) was used. The Shedlovsky function (Equation 3) was chosen for systems with low solubilities, and therefore comparatively low conductances, where corrections due to solvent conductance introduce enough of an uncertainty to preclude application of the more precision-sensitive Fuoss-Onsager theory.

Table VII contains limiting equivalent conductances,  $\Lambda_o$ , association constants,  $K_A$ , and their standard deviations for all the electrolyte-solvent combinations studied as well as ion-size parameters,  $a_J$ , derived from J values for systems analyzed by Equations 1 or 2. Systems for which no  $a_J$ 's are listed in Table VII were analyzed by Equation 3. The association constants for the LiCl solutions are consistently lower than those of KCl and CsCl in ethanol-water mixtures reported by Hawes and Kay (9). This is in agreement with previously reported observations that the association of alkali halides in hydrogen-bonding solvents increases with increasing atomic number (9). For LiCl the plot of log  $K_A$  vs. 1/D is linear and the literature value for 100% ethanol (12) falls on the straight line. Linear plots of log  $K_A$  vs. 1/D are obtained also for TAB BPh<sub>4</sub>, TABPi, and KPi, but of the corresponding literature values for methanol solutions (3), only KPi falls close to the straight line for ethanol-water mixtures.

According to Coplan and Fuoss (3), limiting equivalent conductances of single ions in nonaqueous solvents can be estimated via the assumption that  $\frac{1}{2}\Lambda_{o}TAB$  BPh<sub>4</sub> =  $\Lambda_{o}TAB^{+} = \Lambda_{o}BPh_{4}^{-}$ . To apply this assumption to our results in a manner which would provide data of general interest, we first interpolated (graphically) the  $\Lambda_{o}$ 's for the electrolytes studied here at even values of weight percentage of ethanol. Then, the  $\Lambda_{o}$ 's for single ions were calculated as follows: Table VII. Conductance Parameters and Constants

w	$\Lambda_o$	$a_J$	$K_{A}$							
LiCl										
43.5 57.1 68.2 77.2 86.6 92.3 100.0 ( <i>1</i> 3)	$\begin{array}{l} 44.70 \ \pm \ 0.02 \\ 40.66 \ \pm \ 0.02 \\ 39.50 \ \pm \ 0.04 \\ 39.25 \ \pm \ 0.01 \\ 39.65 \ \pm \ 0.02 \\ 39.98 \ \pm \ 0.01 \\ 39.94 \end{array}$	$\begin{array}{l} 2.10 \ \pm \ 0.16 \\ 2.47 \ \pm \ 0.11 \\ 2.35 \ \pm \ 0.22 \\ 3.33 \ \pm \ 0.03 \\ 3.35 \ \pm \ 0.07 \\ 3.73 \ \pm \ 0.05 \\ 4.4 \end{array}$	$\begin{array}{rrrr} 2.5 & \pm & 0.2 \\ 3.1 & \pm & 0.2 \\ 4.8 & \pm & 0.8 \\ 7.6 & \pm & 0.2 \\ 10.5 & \pm & 0.5 \\ 15.7 & \pm & 0.4 \\ 27 \end{array}$							
	К	Pi								
27.7 53.1 62.0 65.5 79.3 84.5 92.3 100.0	$51.40 \pm 0.05 \\ 39.21 \pm 0.02 \\ 38.96 \pm 0.02 \\ 38.70 \pm 0.05 \\ 40.79 \pm 0.04 \\ 42.60 \pm 0.03 \\ 46.41 \pm 0.03 \\ 50.58 \pm 0.01 \end{cases}$	$ \begin{array}{r} 12.3 \pm 9.5 \\ 14.9 \pm 1.4 \\ 2.24 \pm 0.21 \\ 5.20 \pm 1.36 \\ \dots \\ \dots$	$\begin{array}{cccc} & & & & \\ & & & & \\ & & & & \\ & & & & $							
50.0	22 66 ± 0.00	0.69 1 0.09	$20.40 \pm 0.09$							
81.8 92.3 100.0	$\begin{array}{r} 23.66 \pm 0.00 \\ 32.66 \pm 0.02 \\ 36.67 \pm 0.01 \\ 45.70 \pm 0.02 \end{array}$	$\begin{array}{c} 0.82 \pm 0.02 \\ 4.83 \pm 0.12 \\ 5.23 \pm 0.13 \\ 3.73 \pm 0.06 \end{array}$	$\begin{array}{c} 20.40 \pm 0.06 \\ 43.9 \pm 0.6 \\ 70.7 \pm 0.8 \\ 99.7 \pm 0.6 \end{array}$							
	TAB	BPh₄								
80.8 92.3 100.0	$\begin{array}{r} 26.54 \ \pm \ 0.01 \\ 32.64 \ \pm \ 0.01 \\ 39.58 \ \pm \ 0.02 \end{array}$	· · · · · · ·	$\begin{array}{ccc} 48 & \pm \ 2 \\ 106 & \pm \ 1 \\ 192 & \pm \ 2 \end{array}$							
	KB	Ph₄								
51.0 70.8 50.1 92.3 100.0	$\begin{array}{r} 35.85 \pm 0.02 \\ 34.44 \pm 0.03 \\ 35.63 \pm 0.03 \\ 40.68 \pm 0.03 \\ 44.07 \pm 0.09 \end{array}$	$\begin{array}{c} 2.61 \ \pm \ 0.84 \\ 4.51 \ \pm \ 0.81 \\ 24.3 \ \ \pm \ 2.0 \\ \ldots \end{array}$	$\begin{array}{ccc} & \dots & & \\ & \dots & & \\ & 17 & \pm 3 \\ 151 & \pm 17 \end{array}$							

Table VIII. Interpolated Equivalent Conductances of Electrolytes and Single lons

w	TAB BPh4 (Calcd.)	TABPi	KPi	KBPh₄	KCl (9)	LiCl
100	39.6ª	45.7	50.6	44.1	45.4	39.9 (12)
90	31.9	37.3	45.2	39.8	44.8	39.8
80	27.4	31.8	41.0	36.6	44.1	39.4
70	23.3	28.1	39.2	34.4	ь	39.4
60	20.8	25.4	38.6	34.0	46.9	40.2
50	19.8	23.4	39.8	36.2	51.3	42.2
	$TAB^+ =$					
	BPh₄⁻	Pi⁻	$\mathbf{K}^+$	C1 <sup>-</sup>	$\mathrm{Li}^+$	
100	19.8	25.9	24.7	20.7	19.2	
90	16.0	21.3	23.9	20.9	18.9	
80	13.7	18.1	22.9	21.2	18.2	
70	11.6	16.5	22.7			
60	10.4	15.0	23.6	23.3	16.9	
50	9.9	13.5	26.3	25.0	17.2	

<sup>&</sup>lt;sup>a</sup> Value determined directly. Remaining  $\Lambda_o$ 's for TAB BPh<sub>4</sub> calculated from  $\Lambda_o$ TABPi +  $\Lambda_o$ KBPh<sub>4</sub> -  $\Lambda_o$ KPi. For 100% ethanol calculated  $\Lambda_o$  is 39.2. <sup>b</sup> Interpolation too uncertain for that composition.

 $\Lambda_{o}Pi^{-} = \Lambda_{o}TABPi - \Lambda_{o}TAB^{+}; \Lambda_{o}K^{+} = \Lambda_{o}KPi - \Lambda_{o}Pi^{-}$ 

 $\Lambda_{o}Cl^{-} = \Lambda_{o}KCl - \Lambda_{o}K^{+}; \ \Lambda_{o}Li^{+} = \Lambda_{o}LiCl - \Lambda_{o}Cl^{-}$ 

The limiting equivalent conductances of electrolytes and of single ions at even solvent compositions are compiled in Table VIII.

The literature values for the limiting equivalent conductances of K<sup>+</sup>, Cl<sup>-</sup>, and Li<sup>+</sup> ions in 100% ethanol determined from transference numbers (7) are 23.55, 21.85, and 17.05, respectively. The corresponding discrepancies between these and our estimated values in Table VIII are 4.6, 5.0, and 7.1%, in that order. The discrepancies would be somewhat smaller if the Kohlrausch value of  $\Lambda_0$ TAB BPh<sub>4</sub> = 39.2 were used in the calculation, instead of the directly determined value of 39.6. For methanol solutions, the Coplan-Fuoss assumption was demonstrated to be valid to better than 1% (3).

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# NOMENCLATURE

- a = ion-size parameter, Angstroms
- $a_J =$  ion-size parameter derived from J values, Angstroms
- C = concentration of electrolyte, moles per liter
- $d_o =$  density of solvent, grams per ml.
- D = dielectric constant of solvent

$$E = \frac{6.7747 \times 10^{12}}{D^3 T^3} - \frac{0.9977 \times 10^8}{\eta D^2 T^2},$$

where T is absolute temperature

- = mean ionic activity coefficient, molar scale  $f_{\pm}{F}$
- $6.308 \times 10^{21} R^3$ , cc., where R is a hydrodynamic radius = of the ion

$$J = \sigma_1 \Lambda + \sigma_2, \text{ where}$$

$$\sigma_1 = \frac{2.22000 \times 10^5}{D^3} [h(b) + 0.9074 + \ln \frac{2.9127 \times 10^8}{D^{1/2}} a]$$

and

$$\sigma_2 = \frac{761.36}{nD^2} + \frac{12.757 \times 10^8}{nD} - \frac{974.8}{nD^2} [1.0170 +$$

$$\ln \frac{2.9127 \times 10^8}{D^{1/2}}a$$

and 
$$h(b) = (2b^2 + 2b - 1)/b^3$$

 $b = 560.37 \times 10^{-8}/aD$ where

- $k_o$  = specific conductance of solvent, mho per cm.
- $K_A$ = ion-pair association constant, liters per mole
- S = Onsager coefficient,  $\alpha \Lambda_o + \beta$ , where

$$\alpha = \frac{0.8204 \times 10^6}{(DT)^{3/2}}$$
 and  $\beta = \frac{82.501}{\eta (DT)^{1/2}}$ 

- $$\begin{split} S_{(z)} &= \text{Shedlovsky function, } \{z/2 + [1 + (z/2)^2]^{1/2}\}^2, \\ &\text{where } z = S\Lambda_e^{-3/2} (C\Lambda)^{1/2} \end{split}$$
- weight % ethanol in mixture with water w =

## **Greek Letters**

- $\gamma$  = degree of ionic dissociation
- = viscosity, poises η
- $\Lambda =$ equivalent conductance at finite concentration, mho/ liter per cm. mole
- $\Lambda_o$ = limiting equivalent conductance, mho/ liter per cm. mole

## LITERATURE CITED

- Accascina, F., Petrucci, S., Fuoss, R.M., J. Am. Chem. Soc. (1)81, 1301 (1959).
- (2)Akerlof, G., Ibid., 54, 1425 (1932).
- Coplan, M.A., Fuoss, R.M., J. Phys. Chem. 68, 1177 (1964). (3)Fuoss, R.M., Accascina, F., "Electrolytic Conductance," (4)
- Interscience, New York, 1959.
- Fuoss, R.M., Onsager, L., J. Phys. Chem. 61, 688 (1957). Fuoss, R.M., Shedlovsky, T., J. Am. Chem. Soc. 71, 1496 (5)(6)(1949).
- (7)Graham, J.R., Gordon, A.R., Ibid., 79, 2350 (1957).
- Graham, J.R., Kell, G.S., Gordon, A.R., Ibid., 79, 2350 (1957). (8)
- (9)
- Hawes, J.L., Kay, R.L., J. Phys. Chem. 69, 2420 (1965). "International Critical Tables," Vol. 5, McGraw-Hill, New (10)York, 1929.
- Jones, G., Bradshaw, B.C., J. Am. Chem. Soc. 55, 1780 (1933). (11)
- Kay, R.L., Ibid., 82, 2099 (1960). (12)
- Osborne, N.S., McKelvey, E.C., Bearce, H.W., J. Wash. Acad. (13)Sci. 2, 95 (1912).
- Popovych, O., Anal. Chem. 38, 558 (1966). (14)
- Popovych, O., Friedman, R.M., J. Phys. Chem. 70, 1671 (15)(1966).
- Shedlovsky, T., J. Franklin Inst. 225, 739 (1938). (16)

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